

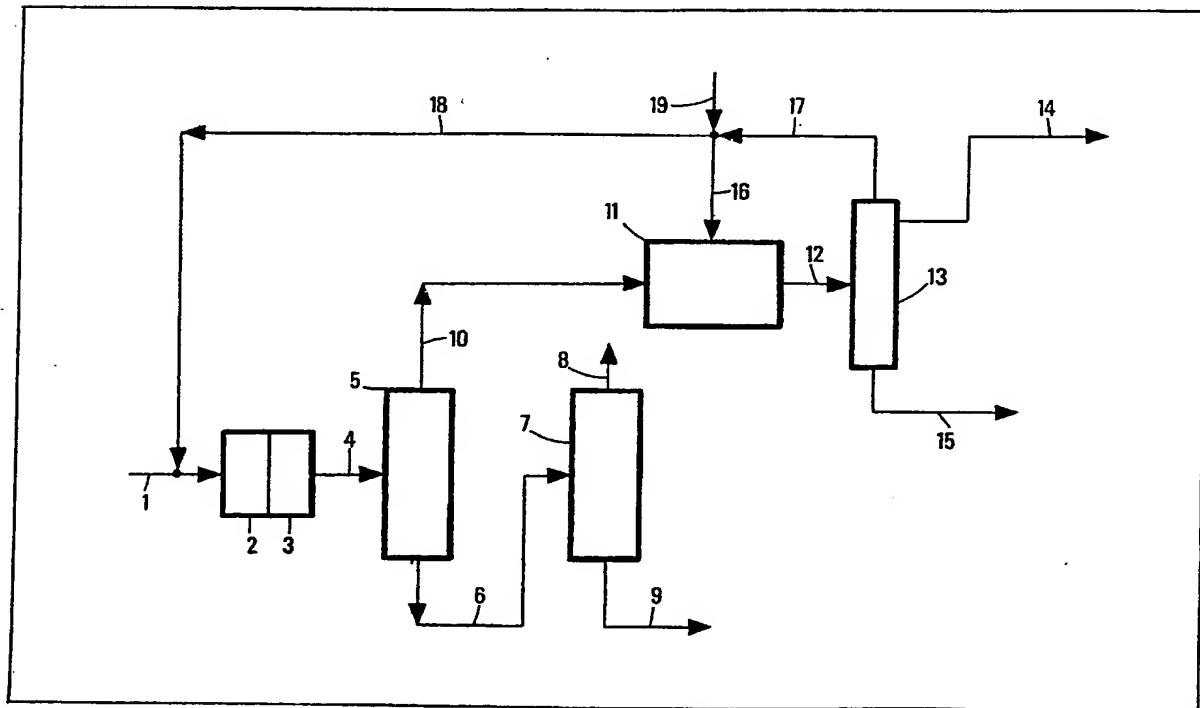
(12) UK Patent Application (19) GB (11) 2 057 006 A

(21) Application No 8027089  
(22) Date of filing 20 Aug 1980  
(30) Priority data  
(31) 7921208  
(32) 21 Aug 1979  
(33) France (FR)  
(43) Application published  
25 Mar 1981  
(51) INT CL<sup>3</sup>  
C07C 2/00 2/04 2/54  
5/23  
(52) Domestic classification  
C5E 222 244 292 303  
310 386 391 CD  
(56) Documents cited  
None  
(58) Field of search  
C5E  
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**(54) A process for upgrading C<sub>4</sub> olefinic cuts**

(57) An olefinic  $C_4$  cut 1 from a cracking or steam cracking unit is upgraded by being subjected to isomerization conditions at 2 so as to convert at least 80% of its 1-butene content to 2-butene, subjecting the so-treated  $C_4$  cut to polymerization

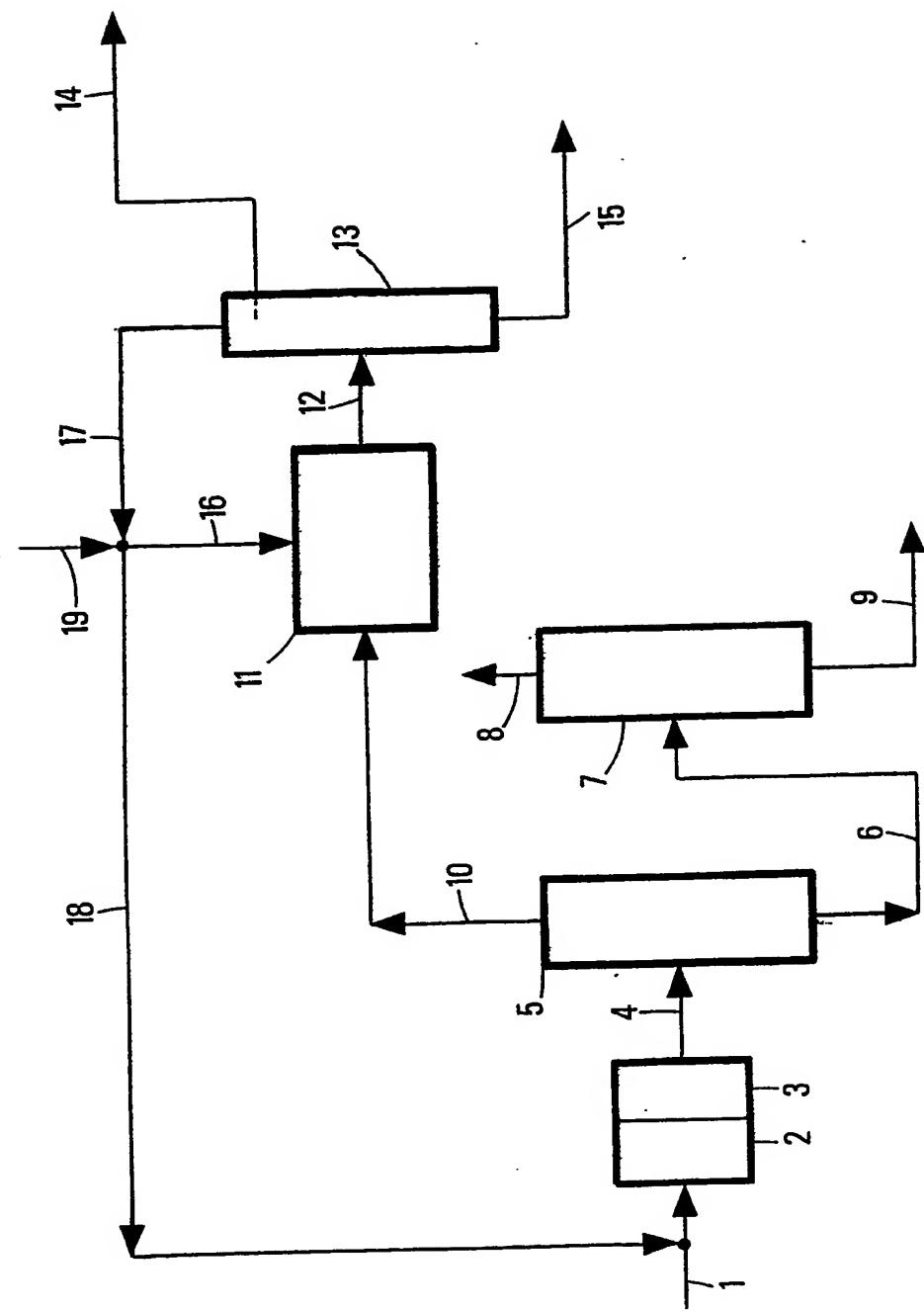
conditions at 3 so as to convert at least 90% of its isobutene content to isobutene dimers and trimers without substantially converting the normal butenes, separating at 5 the isobutene dimers and trimers through 6, alkylating the remaining fraction at 11 and fractionating the latter to an alkylate 15, L P G 14 and an isobutane-containing fraction 17.



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## SPECIFICATION

A process for upgrading C<sub>4</sub> olefinic cuts

The development of various processes of steam cracking and catalytic cracking of naphthas and gas-oils results in the supply on the market of a C<sub>4</sub> cut which, after butadiene extraction, essentially 5 contains a mixture of butenes, isobutene, butane and isobutane which it is desirable to upgrade.

The olefins, butenes and isobutene can be used for the synthesis of more elaborated petrochemical products (alcohols, aldehydes, acids, nitriles, etc.), but the available amounts of these C<sub>4</sub> 10 cuts are generally too large or at least may become too large for having recourse only to this way to upgrade the C<sub>4</sub> cuts.

10 A second way consists of recycling said C<sub>4</sub> cut to the cracking unit (steam cracking) or to the catalytic cracking unit, after hydrogenation of the olefins; but, in this case, the isobutane contained in the hydrogenated cut, which amounts to more than 50% by weight of said cut, does not give sufficient 15 ethylene yields and also results in a substantial production of methane which practically can be used only as fuel.

15 A third way to upgrade said C<sub>4</sub> cut consists, after hydrogenation thereof, of separating the n-butane from the isobutane by distillation and recycling to the steam-cracking unit only the n-butane, while recovering the isobutane for more advantageous uses, such for example as the production, by 20 alkylation, of isoparaffinic gasolines. However, the yields of ethylene and propylene in a steam-cracking unit conducted in this manner, do not exceed respectively 38 and 20% by weight and the methane 25 production amounts to about 25% by weight.

20 A fourth way of upgrading the C<sub>4</sub> cut consists of alkylating the olefins of said cut with the isobutane contained therein, so as to obtain the maximum yield of gasoline. However, in said alkylation step the behaviour of isobutene is less favorable than that of the butenes for obtaining gasoline of high 25 octane number; as a matter of fact, the Research (or Clear) octane numbers of the normal butene alkylates are higher than those of the isobutene alkylates.

25 In order to improve this fourth way, it is possible, in a first stage, to subject the C<sub>4</sub> cut to polymerization during which an effort is made to limit the total conversion of the normal butenes contained in the cut to less than 10% and during which at least 90% of the isobutene is converted (preferably, at least 92% of the isobutene is converted); this hydrocarbon is converted essentially to 30 isobutene dimers and trimers; subsequently, the resulting product is subjected to a fractionation so as to obtain, on the one hand, a first fraction which is fed to the alkylation unit and, on the other hand, a second fraction which is supplied to the gasoline pool, after partial or total hydrogenation thereof. The first fraction, fed to the alkylation stage contains in major part butane and isobutane and the butenes which have not reacted during the polymerization. Such a process is described in the British Patent 35 35 Specification No. 2,017,746.

35 The present invention is an improvement to the process disclosed in the British Patent Specification No. 2,017,746 for upgrading the C<sub>4</sub> cut, and consists of subjecting the C<sub>4</sub> olefinic cut, not to a mere polymerization reaction as above-described, but to a so-called "isomerizing polymerization", which reaction provides not only for a selective conversion of isobutene to C<sub>8</sub> dimers and C<sub>12</sub> trimers, 40 but also for the displacement of the double bond of 1-butene, whereby the major part of 1-butene is converted to 2-butene, thereby obtaining, under the selected operating conditions and catalysts, a composition close to that corresponding to the thermo-dynamic equilibrium. The other constituents of the charge are not substantially converted during the isomerization reaction. This conversion of 1-butene to 2-butene is of prime importance for the alkylation reaction performed after the fractionation 45 of the polymerization effluent, since the products obtained by alkylation of 2-butene have an octane number clearly higher than that of the alkylates issued from 1-butene (the alkylates obtained from 2-butene have a R.O.N. from 5 to 7 points higher than that obtained from 1-butene).

45 The operating conditions are such that the normal butenes contained in the fraction fed to the alkylation zone contain by weight at least 85% of 2-butene and that, during the isomerization, at least 50% of the 1-butene is converted to 2-butene.

50 The process according to the invention is diagrammatically illustrated by the accompanying drawing. By the process of the invention, it is possible to obtain a polymerate which does not require any particle or total hydrogenation, in view of the high quality of said polymerate.

55 The hydrogen feeding duct is not shown.

The olefinic C<sub>4</sub> cut is fed, through line 1, to the hydroisomerization zone 2 where takes place the isomerization of the double bond of the normal butenes. This hydro-isomerization is performed in the presence of a catalyst used as a fixed bed or a moving bed or a fluidized bed, at a temperature from about 0 to 250°C, under a pressure from about 0.1 to 20 MPa and at a liquid hydrocarbon flow rate (space vel. city) of about 0.2 to 20 volumes of hydrocarbon per volume of catalyst and per hour. The 60 catalyst contains generally at least one metal, preferably from group VII of the periodical classification of elements (for example cobalt, nickel, palladium, etc.) deposited on a carrier of low acidity, for example transition alumina, silica, etc., having a specific surface from about 20 to 300 m<sup>2</sup> per gram and a pore volume from about 0.20 to 0.80 cc per gram.

The acidity of the carrier may be determined by the known test of ammonia adsorption, described

in "Journal of Catalysis, 2, 211—222 (1963): this method consists of heating the carrier to 600°C under a vacuum (i.e. under a pressure lower than about 1 Pa) up to a complete gas removal; then, the carrier is placed in a calorimeter at 320°C and ammonia is introduced in such an amount that the final pressure of the system at equilibrium attains 40 kPa and the evolved heat is then measured.

5 The selected carriers have a neutralization heat, by ammonia adsorption, of less than 10 calories per gram at 320°C under a pressure of 40 kPa and preferably less than 7 calories per gram. the neutralization heat of the final catalyst is substantially identical, i.e. less than 10 calories per gram and, preferably, less than 7 calories per gram. 5

The catalyst may optionally operate in sulfided medium (for inhibiting the hydrogenation properties of the metal), but this is not obligatory. In order to avoid a loss in the catalytic properties of the solid and also to avoid secondary reactions, it is preferably to conduct the reaction under a hydrogen partial pressure, the hydrogen being introduced with the charge. The ratio hydrogen/hydrocarbon is then generally from 0.01 to 2 (ratio expressed in moles by mole). 10

10 At the outlet of the hydro-isomerization zone 2, the totality of the effluent enriched with 2-butene properties of the metal), but this is not obligatory. In order to avoid a loss in the catalytic properties of the solid and also to avoid secondary reactions, it is preferably to conduct the reaction under a hydrogen partial pressure, the hydrogen being introduced with the charge. The ratio hydrogen/hydrocarbon is then generally from 0.01 to 2 (ratio expressed in moles by mole). 10

15 (>85% of 2-butene with respect to the total content of normal butenes in said effluent) is fed to a polymerization zone 3 which may be located either in a second reactor, after the isomerization reactor 2, or in the reactor already used for the isomerization, the separate isomerization and polymerization catalyst beds being then generally superposed. 15

15 It must be observed that the effluent from the hydro-isomerization zone contains a hydrogen excess which has not been used during the isomerization and said hydrogen excess also passes through the polymerization zone without producing any disturbance of said polymerization reaction. 20

20 In the polymerization zone, the conditions are such that the isobutene reacts up to conversion rates higher than 90% by weight while the total conversions of normal butenes (1-butene and cis-and trans-2-butenes) remain lower than or equal to 10% by weight and preferably lower than 7%. 20

25 The polymerization reactions are generally performed in the presence of a catalyst used, for example, in a fixed bed, at a temperature of from about 30 to 400°C, under a pressure from about 0.1 to 20 MPa (1 to 200 bars), (preferably the temperature is from about 80 to 150°C and the pressure from 2 to 6 MPa) at a liquid hydrocarbon flow rate (space velocity) of from about 0.05 to 5 volumes per volume of catalyst and per hour. 25

30 The acid type catalyst may be a silica-alumina or a boron alumina or a borated alumina. It is also possible to select a catalyst obtained by treatment of a transition alumina with an acid fluorine derivative, optionally with the addition of a silicic ester. According to the present invention, the catalyst used in the polymerization reaction exhibits qualities superior to those of other polymerization catalysts such as phosphoric acid on Kieselguhr or on silica, or on quartz, or such catalysts as those of the "solid phosphoric acid" type, i.e. catalysts consisting of a siliceous material of high adsorbing power, impregnated with a high proportion of phosphoric acid, or still such as alumina and thoria gel mixtures, either co-precipitated or not, with optional additions of chromium oxide, zinc oxide or oxide of an equivalent metal. 30

35 Preferably, according to the invention, there is used silica-alumina whose silica content is from 60 to 95% by weight and preferably from 70 to 90%, and preferably containing as additive from 0.1 to 5% by weight of zinc oxide. In view of the high exothermicity of the conversion, it is preferable that the isobutene content of the charge be lower than about 35% by weight, since otherwise the charge must be diluted for example with butane or isobutane, and/or, for example, with a portion or the totality of the butene and/or the isobutene issuing through line 17 from the effluent of the hereunder-defined alkylation zone 11. This recycled fraction of butane and/or isobutane is fed either to the polymerization zone 3, when the polymerization reactor is independent from the isomerization reactor 2, or (case of the figure) at the inlet of the unique reactor. In the case of a unique reactor with two different beds, one for hydro-isomerization and the other for polymerization, the recycled portion may be supplied directly to the inlet of said second catalyst bed so as to avoid too high temperature increase. 40

40 45

50 Preferably, the temperatures, pressures and VVH are substantially the same in the hydro-isomerization and polymerization reaction zones. At the outlet of the polymerization zone, the totality of the reaction mixture i.e. unconverted butenes, unconverted isobutene, isobutene dimers and trimers, butane and dilution butane, isobutane, etc. are conveyed through line 4 to a fractionation zone 5 wherefrom there are withdrawn mainly, through line 10, a first fraction containing a major part of the butane, the isobutane, the isobutene and the butenes and through line 6, a second fraction mainly containing isobutene dimers and trimers. This second fraction is fed to a second fractionation zone 7, wherefrom is withdrawn, at the top, through line 8, a mixture or "poly" gasoline containing a major portion of isobutene dimers and trimers (30 to 70% by weight of dimers and 70 to 30% by weight of trimers, the proportions being expressed in percent of said mixture) which is fed, without requiring hydrogenation, to the gasoline pool, and at the bottom, through line 9, a residue having an initial boiling point higher than 200°C which can be fed to a fuel oil pool. The fraction withdrawn through line 10 from the fractionation zone 5 is fed to an alkylation zone 11. 50

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65 Generally, the alkylation reaction is performed either in the presence of a dissolved catalyst, i.e. in liquid phase, or in the presence of a solid catalyst, preferably used as a fixed bed, at a temperature from —20 to 200°C and under a pressure from 10 kPa to 20 MPa. It is thus possible to proceed in the liquid 60

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phase in the presence of a strong inorganic acid such as hydrofluoric acid or sulfuric acid, with or without addition of a Lewis acid such as boron trifluoride or antimony pentafluoride or still aluminum trichloride, and/or in the optional presence of a Brönsted acid. It is still possible to proceed in the vapor phase in the presence of a solid catalyst of the type of the phosphates, arsenates or stannates of 5 polyvalent metals with boron trifluoride added thereto. Alkylation processes are also known, which are performed in the presence of catalysts having a zeolitic structure, with molecular sieves, in the presence or not of silica-aluminas, for example with the optional presence of at least one metal such as nickel, palladium, rhodium, platinum, etc.

More particularly, the alkylation reaction may be performed at temperatures close to room 10 temperature and under moderate pressures.

An additional isobutane amount can be added to the alkylation zone 11 through line 16. This additional amount is preferable in order to obtain, at the inlet of the alkylation zone, a suitable molar ratio isobutane/olefins in the range from 6/1 to 10/1, this ratio being selected to obtain an alkylate of optimum octane number. The isobutane of line 16 comes from line 17 and/or 19.

15 There is so obtained, during the alkylation, an alkylate which is withdrawn from line 12 and which 15 can be fractionated in zone 13 in order to obtain:

a) — LPG, which are withdrawn through line 14, usually containing saturated hydrocarbons (iso and normal paraffins) having 4 carbon atoms per molecule, i.e. butanes of high isobutane content, which can be fed to the gasoline pool.

20 b) — An optional fraction (line 17) of high isobutane content, withdrawn from the top of the fractionation zone 13 and which is fed, according to the needs, to the polymerization zone 3, through line 18 (on the figure line 18 is connected to the inlet of the isomerization zone 2 as above-mentioned) so as to avoid therein too high temperature increases and/or to the alkylation zone 11, through line 16 and.

25 c) — An alkylate which can be used, for example, as motor fuel, since the alkylation products generally have a clear octane number from 88 to 95. This alkylate is recovered through line 15.

Additional isobutane (necessary for diluting the charge and of diluting the cut fed to the alkylation zone) may be introduced through line 19.

30 According to a preferred embodiment of the invention, the alkylate of line 15 and the "poly" gasoline of line 8 are collected together.

#### EXAMPLE 1

This example relates to the treatment of an olefinic C<sub>4</sub> cut from steam cracking; the charge composition is given in Table I.

TABLE I

CHARGE COMPOSITION (% BY WEIGHT)	
Isobutane	2
N-butane	10
Isobutene	46
1-butene	24
2-butenes	18

This charge is treated in an isomerizing polymerization zone consisting of two successive catalyst fixed beds (2 and 3 on the figure); in the first bed, where takes place the hydro-isomerization, the catalyst is that commercialized under reference LD 265 by Protacalyse Corporation; this catalyst is made of alumina of high purity containing 0.3% by weight of palladium. Its specific surface is 60 m<sup>2</sup>/g, 40 its total pore volume is 0.50 cc/g, its filling density is 0.7 g/cc. It has the form of balls of a diameter of 2 40 to 4 mm. The neutralization heat of this catalyst, measured under the above-mentioned conditions, is 6 calories per gram.

In the second bed, where takes place the polymerization, the catalyst is a silica-alumina sold on the trade as being of the Durabeat Perl Catalysator Neu type manufactured by Kalichemie Corporation, 45 containing 0.2% by weight of zinc.

The operating conditions, in each of the two isomerization and polymerization zones, are as follows:

	VVH (in $h^{-1}$ )	2	
	T °C	110	
5	Pressure MPa	4	5

In the hydro-isomerization zone, the ratio  $H_2/HC$  is 0.5.

The Table II below reports the composition of the outlet effluent from the isomerization zone as well as the effluent composition at the outlet of the polymerization zone. In the isomerization zone, 82.5% by weight of 1-butene have been converted to 2-butenes.

TABLE II

	ISOMERIZATION EFFLUENT % b.w.	POLYMERIZATION EFFLUENT % b.w.
Isobutane	2	2
N-butane	10	10
Isobutene	46	4.5
1-butene	4.2	3.8
2-butenes	37.8	34
$C_5 - C_{12}$ cuts (poly)	—	42.1
Fuel-oil	—	3.6

After fractionation of the polymerization effluent in zone 5 of the figure, there is recovered, through line 10, normal butane, isobutane, isobutene and 1 and 2-butenes. This fraction is fed to the alkylation zone 11. However, in this cut, the isobutene proportion is insufficient (3.7% of isobutane for 80% of olefins) to obtain a molar ratio isobutane/olefins of at least 6, which is the minimum value

15 required to avoid secondary reactions. Through line 16, there is added an additional amount of isobutane corresponding to 6.2 times the weight of the charge introduced through line 10. The molar ratio isobutane/olefins is then equal to 8.

The alkylation reaction is conducted in the presence of hydrofluoric acid, in reactor 11, stirred and cooled in such a manner as to maintain the temperature of the reaction mixture at 30°C. The other 20 operating conditions are as follows:

- pressure: 1.5 MPa
- ratio isobutane/olefins: 8 (molar)
- hydrofluoric acid volume (at 85% by weight) per hour and per volume of olefin: 2
- ratio by volume of acid to hydrocarbons: 1

25 After decantation, separation, washing and distillation of the reaction effluent, there is obtained (in proportion to the charge fed through line 10):

1) — through line 15: 83.8% by weight (with respect to the initial olefinic  $C_4$  cut of line 1) of gasoline alkylate;

2) — through line 14: 10% by weight of LPG containing unreacted butane;

30 3) — through line 17: the isobutane excess which is recycled, partly to the alkylation zone 11 through line 16, and partly to the polymerization zone 3 through line 18 which, in the embodiment shown in the figure, is connected, as explained above, to the inlet of the isomerization zone and is used to dilute the fresh charge, since the latter contains more than 35% of isobutene as above explained.

There is so added to the fresh charge 44.2% by weight of isobutane (dilution isobutane). For sake of 35 simplification of Table II, the dilution isobutane has not been taken into account in the reported results.

Since the charge to be treated in the present example has an insufficient isobutene content, it is

necessary to use higher amounts of isobutane by adding isobutane (amounting to 78% by weight with respect to the charge in line 1) through line 19.

The balance of the process with respect to the 100% of the charge and the 44.2% of dilution isobutane, but without taking into account the additional isobutane required in the alkylation reaction (additional amount fed through line 16) is as follows by weight:

5	— LPG	10%	5
	— Alkylate (line 15)	83.8%	
	— "poly" gasoline	42.1%	
	— Fuel-oil	3.6%	
10	— Products from line 17	4.7%	10

The obtained gasolines have the following octane numbers:

	RON	Ethylated RON	MON	Ethylated MON
— Alkylate	95	108.5	91.5	106.6
— "Poly" gasoline	102	105.5	85	88
— Alkylate and "poly" gasoline mixture	97.6	107.9	89.6	100.7

The octane number of the mixture shows a "synergistic" effect between the components of the mixture, since the theoretical octane numbers are as follows:

15 — RON:

$$95 \times \frac{83.8}{83.8 + 42.1} + 102 \times \frac{42.1}{83.8 + 42.1} = 96.34$$

— Ethylated RON:

$$108.5 \times \frac{83.8}{83.8 + 42.1} + 105.5 \times \frac{42.1}{83.8 + 42.1} = 107.50$$

— MON:

$$20 \quad 91.5 \times \frac{83.8}{83.8 + 42.1} + 85 \times \frac{42.1}{83.8 + 42.1} = 89.32 \quad 20$$

— Ethylated MON:

$$106.5 \times \frac{83.8}{83.8 + 42.1} + 88 \times \frac{42.1}{83.8 + 42.1} = 100.32$$

It is thus preferable to recover together the alkylate and the "poly" gasoline.

#### EXAMPLE 2

25 This example concerns the treatment of an olefinic C<sub>4</sub> cut from catalytic cracking in the same equipment, under the same conditions, and with the same catalysts as in the preceding example.

The composition in % by weight of said C<sub>4</sub> cut is as follows:

5	— Is butane	35	5
	— n-butane	12	
	— isobutene	16	
	— 1-butene	10	
	— 2-butenes	27	

In the following Table III, the compositions of the effluent at the outlet of the hydro-isomerization zone is indicated as well as the composition of the effluent at the outlet of the polymerization zone.

TABLE III

	ISOMERIZATION EFFLUENT % b.w.	POLYMERIZATION EFFLUENT % b.w.
Isobutane	35	35
n-butane	12	12
isobutene	16	1.5
1-butene	3.7	3.3
2-butenes	33.3	30
"poly" gasoline (C <sub>6</sub> —C <sub>12</sub> )	—	16.8
fuel-oil	—	1.4

10 After distillation of the polymerization effluent, there is recovered (a) a "poly" gasoline fraction, (b) 10 a fuel oil fraction and (c) at the top, the olefinic C<sub>4</sub> fraction enriched with 2-butenes, which is alkylated by means of isobutane with a ratio iso C<sub>4</sub>/olefin of 8, obtained by the addition of isobutene, but, in the present example, this isobutane addition is only required for the starting period since the cut contains fairly enough of isobutane to satisfy the requirements of the alkylation reaction (35% by weight of 15 isobutane for 34.9% of olefin). The other operating conditions are the same as in Example 1. 15

The balance of the process with respect to the 100% of the charge and the 2.9% of dilution isobutane added to the fresh charge through line 18, but without taking into account the additional isobutane required for the alkylation reaction, is as follows by weight:

20	— LPG	12%	20
	— Alkylate	68.7%	
	— "poly" gasoline	16.7%	
	— Fuel oil	1.4%	
	— Product from line 17	4.1%	

The obtained gasolines have the following octane numbers:

	RON	Ethylated RON	MON	Ethylated MON
— Alkylate	95	108.5	91.5	106.5
— "Poly" gasoline	102	105.5	85	88
— Alkylate and "poly" gasoline mixture	96.6	108	90.5	103

**EXAMPLE 3**  
(Comparative)

5 The charge of Example 1 is treated without making use of the hydro-isomerization zone 2. In other words, the charge passes directly to zone 3 without addition of the hydrogen required for the hydro-isomerization. The other operating conditions are unchanged. 5

The balance of the process with respect to the totality of the charge (100%) and the 44.2% of dilution isobutane, is given below. The results of Example 1 are given into brackets:

10	— LPG	10 (10)	10
	— Alkylate	80.7 (83.8)	
	— "Poly" gasoline	42.1 (42.1)	
	— Fuel oil	3.7 (3.6)	
	— Total products	136.5 (139.5)	
15	— Losses	7.7 (4.7)	15

Octane number of the obtained product (into brackets, the octane numbers obtained according to Example 1):

	RON	Ethylated RON	MON	Ethylated MON
— Alkylate	92.5 (95)	105.5 (108.5)	89.5 (91.5)	104.5 (106.5)
— "Poly" gasoline	102 (102)	105.5 (105.5)	85 (85)	88 (88)
— Alkylate and "poly" gasoline mixture	95.5 (97.6)	105.5 (107.9)	88 (89.6)	99 (100.7)

20 It is observed that the octane numbers of the mixtures are not so good as the calculated theoretical octane numbers of Example 1. Furthermore in the present case, it would be more convenient 20 to hydrogenate the "poly" gasoline in order to improve its qualities.

**EXAMPLE 4**  
(Comparative)

25 The charge of Example 2 is treated without making use of the hydro-isomerization zone 2. In other words, the charge passes directly to zone 3. The other operating conditions remain unchanged. The 25 balance of the process with respect to the totality of the charge and the 2.9% of dilution isobutane is given below: (into brackets the results of Example 2).

— LPG	12 (12)
— Alkylate	67 (68.7)

— "Poly" gasoline	17.1 (16.7)
— Fuel-oil	1.5 (1.4)
— Total product	97.6 (98.8)
— Losses	5.3 (4.1)

5 The obtained gasolines, useful as motor fuel, have the following octane numbers (into brackets, the octane numbers obtained in Example 2):

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	RON	Ethylated RON	MON		Ethylated MON
			MON	Ethylated MON	
— Alkylate	94 (95)	107.5 (108.5)	91 (91.5)	106 (106.5)	
— "Poly" gasoline	102 (102)	105.5 (105.5)	85 (85)	88 (88)	
— Alkylated and "poly" gasoline mixture	95.5 (96.5)	107 (108)	90 (90.5)	102.5 (103)	

The advantage of the process according to the present invention clearly appears from the comparison of the 4 Examples. Not only better yields of gasoline, useful as motor fuel, are obtained, but 10 also the obtained gasolines are of higher quality.

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#### CLAIMS

1. A process for upgrading an olefinic cut essentially containing hydrocarbons with 4 carbon atoms per molecule and issued from a cracking or steam cracking unit, said process being remarkable in that:

15. a) — the olefinic cut is fed to a hydro-isomerization zone where the cut is treated in the presence of hydrogen and of an isomerization catalyst containing at least one metal from group VIII of the periodic classification of elements, deposited on a carrier, under such conditions that at least 80% of 1-butene of said cut are isomerized to 2-butenes, the percentages of the other components of the cut being essentially unchanged and that, at the end of the isomerization reaction, the normal butenes 15 contained in the hydro-isomerization effluent consist of at least 85% by weight of 2-butenes and less than 15% of 1-butene.

20. b) — the totality of the effluent from the hydro-isomerization zone is fed, without being subjected to any intermediary fractionation, to a catalytic polymerization zone in the presence of a catalyst different from the hydro-isomerization catalyst and selected from the group consisting of fluorinated 20 aluminas, boron aluminas and silica-aluminas, so that, on the one hand, at least 90% of the isobutene contained in the hydro-isomerization effluent is converted, in major part, to isobutene dimers and trimers and, on the other hand, the total conversions of the normal butenes contained in the cut remain lower or at most equal to 10% by weight, the butane and isobutane contained in the effluent of the hydro-isomerization zone being substantially unconverted.

25. c) — the effluent from the polymerization zone is fed to a fractionation zone to recover mainly, on the one hand, a fraction containing, in major part, isobutene dimers and trimers and, on the other hand, a fraction containing, in major part, isobutane, butane and butenes, said fraction being fed to an alkylation zone, the alkylation effluent being supplied to a fractionation zone so as to obtain (a) an alkylate, (b) LPG having a high content of saturated hydrocarbons having 4 carbon atoms per molecule 25 and (c) a fraction consisting mainly of isobutane.

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2. A process according to claim 1, wherein, in addition, in step (d) the alkylate, on the one hand, and the isobutene dimers and trimers mixtures, on the other hand, are collected together as gasoline.

3. A process according to claim 1, wherein the catalyst in the hydro-isomerization zone has a neutralization heat, by ammonia adsorption, lower than 10 calories per gram at 320°C under a pressure

40. of 40 kPa.

4. A process according to claim 3, wherein the catalyst carrier of the hydro-isomerization zone is alumina.

45. 5. A process according to claim 1, wherein the olefinic cut, when containing at least about 35% by weight of isobutene, is diluted with an additional amount of isobutane and/ or at least a fraction of the butane and/or isobutane from said fraction consisting mainly of isobutane, recovered by fractionation f the alkylation effluent.

6. The process according to claim 1, wherein said metal from group VIII is selected from cobalt, nickel and palladium.

7. A process according to claim 6, wherein the metal is palladium.

8. A process according to claim 1, wherein the hydro-isomerization reaction is conducted between 0 and 250°C under a pressure of from about 0.1 to 20 MPa, with a liquid hydrocarbons flow rate of about 0.2 to 20 volumes of hydrocarbons per volume of catalyst and per hour, and wherein the polymerization reaction is conducted at a temperature from 30 to 400°C under a pressure from about 0.1 to 20 MPa, with a liquid hydrocarbons flow rate of about 0.05 to 5 volumes per volume of catalyst and per hour. 5

9. A process according to claim 8, wherein the polymerization reaction is conducted at 80 to 150°C, under a pressure from 2 to 6 MPa. 10

10. A process according to claim 8, wherein the temperature, pressure and hydrocarbons flow rate conditions are substantially the same for the hydro-isomerization as for the polymerization.

11. A process according to claim 1 carried out substantially as hereinbefore described in Examples 1 or 2. 15

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1981. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.